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Magnetic and transport measurements on the layered III-VI diluted magnetic semiconductor $In_{1-x}Mn_xSe$

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Magnetic and transport properties of single-crystalline $In_{1-x}Mn_xSe$ ($x=0.01$ and 0.10) have been measured. $In_{1-x}Mn_xSe$ exhibits a prominent magnetization hysteresis between 90 and 290 K. $In_{1-x}Mn_xSe$ is conducting with increasing resistance at low temperatures and a small hysteresis between 90 and 290 K with the cooling trace having lower resistivity. The magnetization above and below the hysteresis is consistent with a paramagnetic signal. A Curie–Weiss fit to the data yields a value of $J_{\mathrm{eff}}/k_B=-240$ K. The data are consistent with a saturated component contributing to the hysteresis and a paramagnetic phase that scales with concentration. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1851408]

I. INTRODUCTION

Layered III-VI diluted magnetic semiconductors (III-VI DMSs) are based on a two-dimensional III-VI semiconductor host ($A^{\mathrm{III}}B^{\mathrm{VI}}$) in which a fraction x of the group-III element is replaced by a transition-metal ion (M). The III-VI DMSs take the form $A^{\mathrm{III}}_{1-x}M_xB^{\mathrm{VI}}$. The III-VI semiconductors GaSe,[1–7] InSe,[3,6–12] GaTe,[13] and GaS (Refs. 14–16) have received considerable interest in the last few years because of their remarkable nonlinear optical properties. Recent work on InSe includes studies on polaron energy-level calculations,[6] pressure dependence of phonons and excitons in InSe films,[8] InSe/Si(111) heterojunctions' electronic structure,[7] and solid InSe structural and electronic properties under pressure.[9]

Although these materials have very desirable optical properties, the pure semiconductors are soft and cannot be easily polished. The InSe structure is shown in the inset of Fig. 1. InSe is two dimensional (similar to mica) with weak van der Waals bonding between the stacked four-atom-thick layers of this crystal.[2] Two middle layers of In ions in $In_{1-x}Mn_xSe$ are sandwiched between top and bottom capping layers of Se ions. Within each four-atom-thick layer, the bonds are covalent. Like the II-VI DMS,[17] substitutional magnetic ions in the III-VI DMS are in a tetrahedral environment. However, each In ion in InSe has only three neighboring Se ions. The fourth neighbor is another In. For substitutional transition-metal ions at the In lattice site, this opens up more complicated exchange channels than was possible in the II-VI DMS.

Suhre *et al.* have shown that the addition of In into GaSe not only strengthens the material enough to allow optical faces to be polished along arbitrary crystalline directions but also enhances the optical characteristics.[4] Additional work on the $In_{1-x}Ga_xSe$ series includes experimental and theoretical studies on the band structure of $In_{1-x}Ga_xSe$ under high pressure.[12]

In this work we present magnetic and transport measurements on $In_{1-x}Mn_xSe$. This builds on recent measurements in $In_{1-x}Ga_xSe$ and expands the exploration of the class of III-VI DMS into the fourth III-VI DMS system investigated to date complementing previous work on $Ga_{1-x}Mn_xSe$,[1] $Ga_{1-x}Mn_xS$,[18,19] and $Ga_{1-x}Fe_xSe$.[20] This class of diluted magnetic semiconductors has already exhibited behavior different from those of the II-VI DMS and III-V DMS that have been studied more extensively.

II. EXPERIMENTAL DETAILS

Single-crystalline $In_{1-x}Mn_xSe$ samples were taken from boules grown by the vertical Bridgman method with nominal concentrations of $x=0.01$ and 0.10. The $x=0.01$ sample was cut in half. One-half was used for the magnetization and the other for transport measurements. Magnetic measurements were taken in a new Quantum Design MPMS XL7 superconducting quantum interference device (SQUID) magnetometer at temperatures between 1.8 and 400 K in fields up to 7 T.

A pure InSe crystal was measured to determine the value of the diamagnetic signal due to the semiconductor host. A diamagnetic susceptibility value of -3.2×10^{-7} emu/g G for InSe has been measured and subtracted from the data.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Magnetization versus temperature measurements taken in a 7-T field on $In_{1-x}Mn_xSe$ samples ($x=0.01$ and 0.10) are shown in Fig. 1. The magnetization increases at low temperature consistent with a paramagnetic phase. As can be seen in Fig. 1, the magnetization scales with concentration with the $x=0.10$ sample a factor of 1.9–2.9 larger than the $x=0.01$ sample. In contrast, the difference in magnetization in the hysteresis loops at 200 K in 7 T is 0.0084 and 0.0083 emu/g for the $x=0.10$ and 0.01 samples, respectively.

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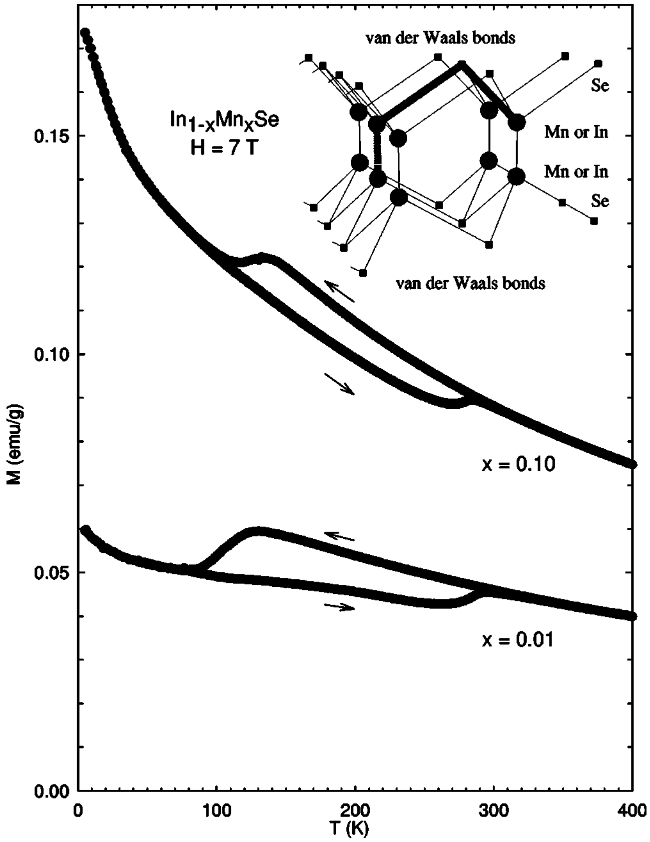

FIG. 1. Magnetization vs temperature measurements for $In_{1-x}Mn_xSe$ ($x=0.01$ and 0.10) in 7 T. Hysteresis is clearly visible between 90 and 290 K. The inset shows a cross section of a single four-atom-thick layer of $In_{1-x}Mn_xSe$, where the large dots are the In lattice sites and the small squares are the Se sites. The Mn–Se–Mn pair is shown by the bold solid line. A direct Mn–Mn pair is shown by the bold dotted line.

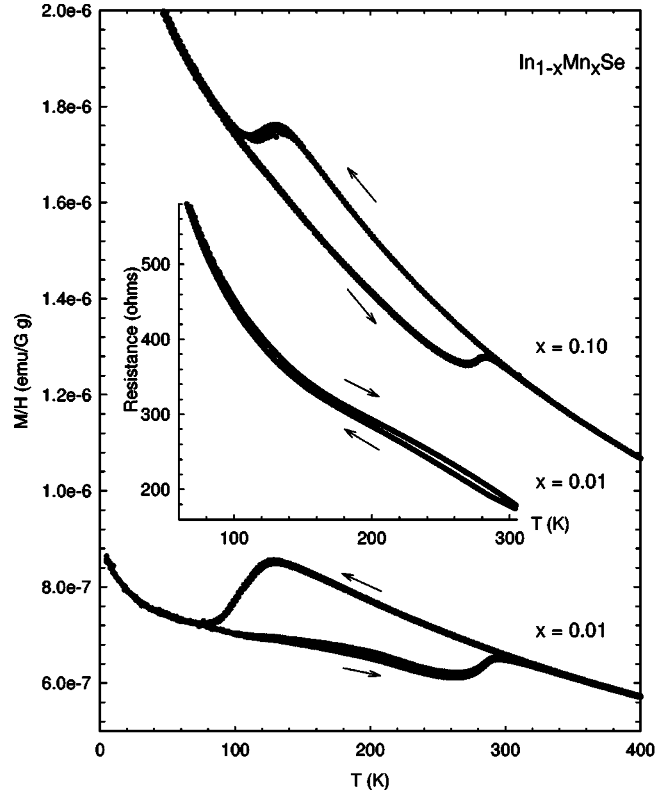

FIG. 2. M/H vs T data for $In_{1-x}Mn_xSe$ ($x=0.01$ and 0.10). Data for the $x=0.01$ sample were taken in a 5-, 6-, and 7-T field. Data for the $x=0.10$ sample were taken in 4, 5, 6, and 7 T. The inset shows the resistance of the $x=0.01$ sample taken in 7 T. The arrows indicate the warming and cooling traces.

Unlike the low-temperature magnetization, the magnitude of the hysteresis does not scale with concentration.

Transport measurements made on the $x=0.01$ sample are shown in the inset of Fig. 2. $In_{1-x}Mn_xSe$ is conducting with increasing resistance at low temperatures, as expected for a semiconductor. A similar hysteresis was observed in $CuIr_2S_{4-x}Se_x$.[21] In $CuIr_2S_{4-x}Se_x$, the magnetization and electrical hysteresis in temperature were accompanied by a structural phase transition from cubic to tetragonal, as determined by x-ray diffraction. Although the changes in resistivity are not as dramatic as those seen in the metal-insulator transition for $CuIr_2S_{4-x}Se_x$, the resistivity data for $In_{1-x}Mn_xSe$ show a small hysteresis between 90 and 290 K with the cooling trace having lower resistivity. The lower resistivity on the cooling trace corresponds to a higher conductivity or larger magnetization while cooling, in agreement with the magnetization data. Although difficult to see on this scale, both the magnetization and resistivity hysteresis loops narrow slightly around 200 K, giving further evidence that the hysteresis loops arise from a common source. Measurements made on pure InSe (not shown) do not exhibit any temperature hysteresis.

If the hysteresis loop in the magnetism arises from Pauli-spin paramagnetism, the magnetization of the hysteresis loop should be linear with field. M/H is plotted as a function of T in Fig. 2. Data for $x=0.10$ in a 4-, 5-, 6-, and 7-T field all collapse to a single curve indicating that the magnetization is linear with field. Similarly, data for the $x=0.01$ sample taken in a 5-, 6-, and 7-T field also collapse.

Examining the data above 300 K as well as the data below 80 K (Fig. 2), we see that the data in these regions also scale linearly with field. We have taken additional $M(H)$ data (not shown) for the $x=0.10$ sample. The magnetization is linear with field up to 7 T at 400, 300, 200, 100, 50, and 20 K. Only slight curvature is evident in the $M(H)$ traces up to 7 T at 10, 5, and 2 K. For paramagnetic materials, the magnetization scales linearly only far away from saturation.

Focusing on the low-temperature magnetization below 80 K (Figs. 1 and 2), the magnetization increases from its value at 80 K as the temperature is reduced to 1.8 K. Figure 3(a) shows the magnetization versus temperature below 15 K in 7 T for the $x=0.10$ sample. At these lowest temperatures, the magnetization flattens and appears to saturate by 1.8 K with a saturation value around 0.176 emu/g. However, at 2 K the magnetization versus field [Fig. 3(b)] reaches a value of 0.176 emu/g but shows no sign of approaching saturation. In fact, the slope at 2 K in 7 T is 2.32×10^{-6} emu/g G. This is similar to the low-temperature behavior previously reported for $Ga_{1-x}Fe_xSe$ (Ref. 20) and $Ga_{1-x}Mn_xS$,[18] and is consistent with Van Vleck paramagnetism (or perhaps with a spin-glass transition at a lower temperature).

A hallmark of the Mn–Se–Mn pairs in the II-VI DMS (e.g., $Cd_{1-x}Mn_xSe$) is the Curie–Weiss behavior in the magnetization from which one can determine the effective inter-

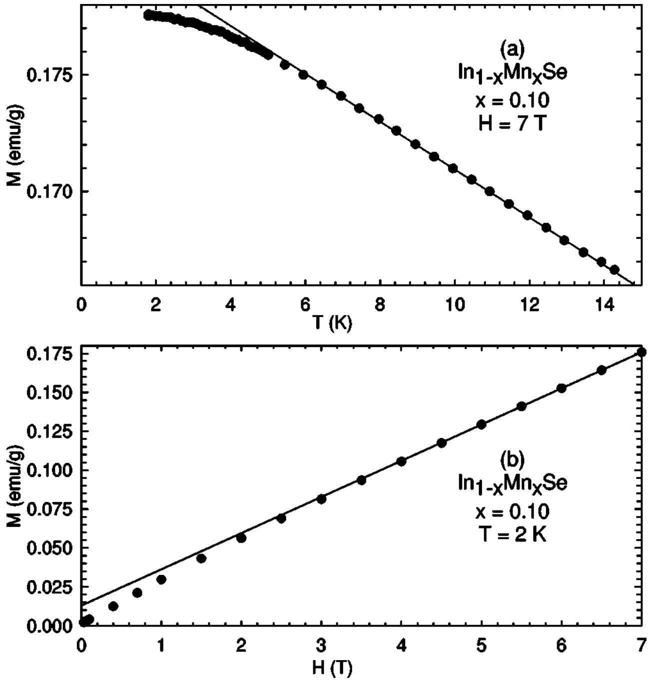

FIG. 3. (a) M vs T in 7 T for the $x=0.10$ sample. The solid line is a guide to the eye showing the flattening of the data at low temperature. (b) M vs H data at 2 K. At 2 K in 7 T, the magnetization is not yet close to saturation.

action strength J_{eff}/k_B. A plot of H/M vs T is shown in Fig. 4 for the data taken in a 1-, 2-, 3-, 4-, 5-, 6-, and 7-T field for the $x=0.10$ $In_{1-x}Mn_xSe$ sample. As can be seen for temperatures on the cooling trace between 150 and 400 K, the data for all fields fall onto a single straight line as one would expect for a Curie–Weiss behavior. In this region, the Curie–Weiss fit to the 7-T data yields $x=0.045$ and $J_{eff}/k_B=-240$ K. The negative sign indicates an antiferromagnetic alignment similar to that observed in many II-VI DMSs. The magnitude of J_{eff}/k_B in $In_{1-x}Mn_xSe$ is somewhat higher than the II-VI DMS where values range over an order of magnitude from −7 to −63 K for the Mn-, Fe-, and Co-based systems. The previously reported value of $J_{eff}/k_B \approx -50$ K for $G_{1-x}Mn_xS$ is also significantly higher than J_{eff}/k_B for similar concentrations in the II-VI DMS.[18] This suggests that there are Mn–Se–Mn (and/or perhaps Mn–Se–In–Mn) pairs in $In_{1-x}Mn_xSe$.

Typically, the actual concentration in a crystal grown by the vertical Bridgman technique is somewhat lower than the nominal value due to solubility limits. The Curie–Weiss fit yields $x=0.045$ for the nominal $x=0.10$ sample. At 50 K in 7 T, the magnetization of the $x=0.01$ sample is a factor of 2.7 smaller than the $x=0.10$ sample. If the magnetization scales with concentration, then the nominal $x=0.01$ sample would have an actual concentration of $x=0.017$.

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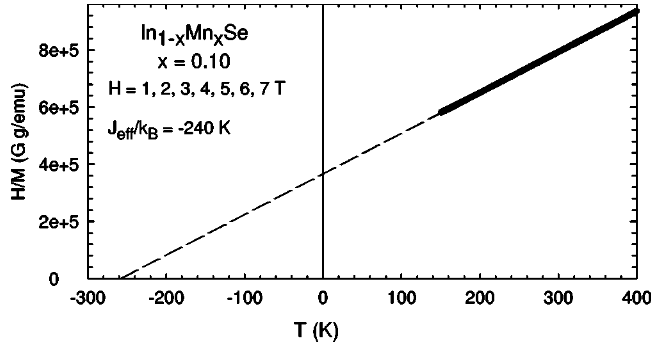

FIG. 4. H/M vs T data for $In_{1-x}Mn_xSe$ in a 1-, 2-, 3-, 4-, 5-, 6-, and 7-T field are shown by the solid circles. For temperatures above 150 K, the data collapse onto a single straight line. A Curie–Weiss fit to the data (shown by the dashed line) yields $x=0.045$ and $J_{eff}/k_B=-240$ K. The negative sign indicates an antiferromagnetic interaction similar to that observed in many II-VI DMSs. This suggests that there are Mn–Se–Mn (and/or perhapse Mn–Se–In–Mn) pairs in $In_{1-x}Mn_xSe$.

[1] T. M. Pekarek, B. C. Crooker, I. Miotkowski, and A. K. Ramdas, J. Appl. Phys. **83**, 6557 (1998).
[2] N. C. Fernelius, Prog. Cryst. Growth Charact. Mater. **28**, 275 (1994).
[3] A. Segura, J. Bouvier, M. V. Andrés, F. J. Manjón, and V. Muñoz, Phys. Rev. B **56**, 4075 (1997).
[4] D. R. Suhre, N. B. Singh, V. Balakrishni, N. C. Fernelius, and F. K. Hopkins, Opt. Lett. **22**, 775 (1997).
[5] S. Meng, B. R. Schroeder, and M. A. Olmstead, Phys. Rev. B **61**, 7215 (2000).
[6] D. E. N. Brancus and G. Stan, Phys. Rev. B **63**, 235203 (2001).
[7] M. O. D. Camara, A. Mauger, and I. Devos, Phys. Rev. B **65**, 205308 (2002).
[8] I. H. Choi and P. Y. Yu, Phys. Rev. B **68**, 165339 (2003).
[9] G. Ferlat, H. Xu, V. Timoshevskii, and X. Blase, Phys. Rev. B **66**, 085210 (2002).
[10] S. Nüsse, P. H. Bolivar, H. Kurz, F. Levy, A. Chevy, and O. Lang, Phys. Rev. B **55**, 4620 (1997).
[11] D. Errandonea, A. Segura, J. F. Sánchez-Royo, V. Muñoz, P. Grima, A. Chevy, and C. Ulrich, Phys. Rev. B **55**, 16217 (1997).
[12] F. J. Manjon, D. Errandonea, A. Segura, and V. Munoz, Phys. Rev. B **63**, 125330 (2001).
[13] J. Z. Wan, J. L. Brebner, and R. Leonelli, Phys. Rev. B **53**, 15413 (1996).
[14] F. J. ManjÓn, A. Segura, and V. Muñoz, J. Appl. Phys. **81**, 6651 (1997).
[15] A. B. M. O. Islam, T. Tambo, and C. Tatsuyama, J. Appl. Phys. **85**, 4003 (1999).
[16] N. Okamoto, T. Takahashi, and H. Tanaka, Appl. Phys. Lett. **73**, 794 (1998).
[17] *Semiconductors and Semimetals*, edited by J. K. Furdyna and J. Kossut (Academic, Boston, 1988), Vol. 25.
[18] T. M. Pekarek, M. Duffy, J. Garner, B. C. Crooker, I. Miotkowski, and A. K. Ramdas, J. Appl. Phys. **87**, 6448 (2000).
[19] C. Fuller, A. Douglas, J. Garner, T. M. Pekarek, I. Miotkowski, and A. K. Ramdas, Phys. Rev. B **65**, 195211 (2002).
[20] T. M. Pekarek, C. L. Fuller, J. Garner, B. C. Crooker, I. Miotkowski, and A. K. Ramdas, J. Appl. Phys. **89**, 7030 (2001).
[21] P. Somasundaram, D. Kim, J. M. Honig, T. M. Pekarek, T. Gu, and A. I. Goldman, J. Appl. Phys. **83**, 7243 (1998).